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The Reactivity of Halogenated Ethers

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

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EASTON, PA.:
MACK PRINTING COMPANY
1926

Accepted by the Department of Chemistry,
June 1926.

ACKNOWLEDGMENT

I beg to acknowledge the invaluable aid and encouragement of Professor Fred Neher, under whose direction this work was begun.

THE REACTIVITY OF HALOGENATED ETHERS

The halogenated ethers resemble the alkyl halides in their reactivity to such reagents as metals, alcoholic and aqueous potassium hydroxide, lime and sodium ethylate. But the reactions of the alkyl halides, as shown by Nef,[1] vary remarkably with temperature, concentration and the nature of the solvent, poor yields and a mixture of products being obtained. The reagent may remove two atoms of the halogen or the halogen acid; unsaturated products may be formed or addition products. An investigation of the behavior of zinc with alcoholic solutions of the halogenated ethers discussed in this paper and others to follow has shown that these compounds are much better suited to a study of the mechanism of the reactions of organic compounds of the halogens since the metal may have an entirely selective action and remove halogen or halogen acid, exclusively. A general mechanism for this selective action has been found by an examination of tetra-, tri-, di- and monochlorodiethyl ethers and some new bromo and bromochloro ethers.

The reactions of the halogenated ethers are more readily interpreted in terms of electron displacement than are those of the alkyl halides and unsaturated hydrocarbons, since the negative alkoxy groups affect the mobilities of both the halogen and the hydrogen atoms of the alkyl radical. Also, there is a sharp differentiation in properties between two isomeric halogenated ethers depending upon the location of halogens on α or β carbon atoms. One may be very unstable and active, the other extremely stable and of very low reactivity.

α,β,β,β-Tetrachlorodiethyl Ether.—Neher and Foster[2] found that an alcoholic solution of this ether reacts with granulated zinc to give a quantitative yield of β,β-dichlorovinyl-ethyl ether; $CCl_3CHClOC_2H_5 + Zn = CCl_2{:}CHOC_2H_5 + ZnCl_2$. No hydrogen is liberated and none of the alcohol adds to the vinyl ether unless the solution is heated. Six molecular proportions of alcohol were used, the mixture cooled under the tap and al-

[1] Nef, *Ann.*, **298**, 330 (1897).

[2] Neher and Foster, *J. Am. Chem. Soc.*, **31**, 413 (1909).

lowed to stand overnight. Later experiments, the results of which have not been published, showed that dichloro-acetal is the chief product when the mixture is heated for several hours on the steam-bath.

To establish the various conditions under which the dichlorovinyl ether may be formed, the work was repeated. It was found that good yields of the unsaturated ether could be obtained with various concentrations of the alcohol solution and at temperatures from about 10° to 50°. Under a wide range of conditions the action of zinc was found to be entirely selective and only chlorine was removed. The removal of hydrogen chloride from the tetrachloro ether would have yielded either trichlorovinyl ether or trichloro-acetal (by the addition of alcohol to the vinyl ether), but there was no indication of the formation of either compound. This reaction of the saturated ether, in which two atoms of chlorine are removed and no hydrogen chloride, is unlike the reactions of the alkyl halides in which zinc usually removes the halogen acid.

α,β,β-Trichlorodiethyl Ether.—This ether was prepared by the addition of dry hydrogen chloride to β,β-dichlorovinyl ether; $CCl_2:CHOC_2H_5 + HCl = CHCl_2CHClOC_2H_5$. A very pure product was obtained by this method since no by-products were formed; no decomposition occurred during the saturation and samples showed only slight coloration after standing for several months. This compound was found to be more reactive toward zinc than the tetrachloro ether. It was thought that this ether would react with zinc to form either the dichlorovinyl ether, $CCl_2:CHOC_2H_5$, or the chlorovinyl ether, $CHCl:CHOC_2H_5$, depending upon the removal of hydrogen chloride or two atoms of chlorine by the zinc. Experiments showed, however, that neither is obtained. Zinc removed hydrogen chloride, exclusively, under all conditions and never two atoms of chlorine, but dichlorovinyl ether could not be obtained, although over 20 different combinations of solvents, concentrations and temperatures were tried with the trichloro ether. In all experiments in which the zinc reacted with the ether alone, or dissolved in indifferent solvents such as carbon tetrachloride, ligroin, toluene or acetone, the reactions were violent, and rapid decomposition could not be prevented by cooling the mixtures to 0°. The resulting products were chiefly tarry masses and no definite compounds could be isolated. When the trichloro ether was dissolved in six molecular proportions of alcohol, however, good yields of dichloro acetal were obtained, hydrogen being evolved throughout the experiments.

$$CHCl_2CHClOC_2H_5 + {}^1/_2\,Zn + C_2H_5OH = CHCl_2CH(OC_2H_5)_2 + {}^1/_2\,ZnCl_2 + {}^1/_2\,H_2$$

The solution of the tetrachloro ether used by Neher and Foster contained six molecular proportions of alcohol, also, and was allowed to react at room temperatures. They obtained no dichloro-acetal under these conditions but did get good yields of the dichlorovinyl ether. When the trichloro ether loses hydrogen chloride the same dichlorovinyl ether is released that

is formed by the removal of two chlorine atoms from this tetrachloro ether, but the formation of dichloro-acetal by alcohol addition could not be prevented even by cooling the solution with an ice-and-salt freezing mixture and adding the zinc very gradually.

The Formation of Vinyl Ethers and Acetals.—In an attempt to find a general mechanism for the selective removal of the halogen or the halogen acid from halogenated ethers and to explain the conditions under which vinyl ethers or acetals are formed, this reaction has been applied to a number of halogenated ethers containing from one to four halogen atoms in the alkyl radical. The following general facts have been determined. (1) Zinc will remove halogen atoms from both carbon atoms only when there are three atoms of the halogen on the beta carbon atom of the halogenated diethyl ether and one or more on the alpha carbon. In alcoholic solution, good yields of vinyl ethers are obtained by this action. (2) The halogen acid will be removed if an alpha carbon atom carries a halogen atom and there are one or more hydrogen atoms on the beta carbon atom. This has been found true for ethers carrying one, two and three hydrogen atoms on the beta carbon atom and one halogen atom on the alpha carbon atom. The product, however, is always an acetal instead of a vinyl ether when the saturated ether loses the halogen acid in the presence of alcohol. (3) A hydrogen atom on an alpha carbon atom is never removed by zinc if there is halogen on this carbon. If there is hydrogen on the beta carbon atom, however, it is always removed with the halogen of the alpha carbon atom, although the beta carbon may carry one or two atoms of the halogen.

The reaction of the trichloro ether mentioned above is typical of all other halogenated diethyl ethers that lose the halogen acid and form acetals in the presence of alcohol. The following examples are similar to the tetrachloro ether reaction and they show that vinyl ethers may be formed in the presence of alcohol if they are released by the removal of two halogen atoms instead of the halogen acid.

α-Chloro-β,β,β-tribromodiethyl Ether.—This compound was made by the action of phosphorus pentachloride on bromal alcoholate in ether solution; $CBr_3CH(OH)OC_2H_5 + PCl_5 = CBr_3CHClOC_2H_5 + POCl_3 + HCl$. An attempt had been made to prepare the corresponding tetrabromo ether by the action of phosphorus pentabromide on the bromal alcoholate, but with no success. The chief product was bromoform instead of the tetrabromo ether. The latter was finally prepared by converting the chlorotribromo ether into dibromovinyl ether by the zinc reaction and adding bromine to the unsaturated ether.

β,β-Dibromovinyl-ethyl Ether.—An alcoholic solution of the chlorotribromo ether, prepared as described above, reacted with zinc to form dibromovinyl-ethyl ether. No hydrogen was evolved; this indicated that only halogen atoms were removed by the zinc and not the halogen acid;

there was no evidence of alcohol addition to form an acetal. $CBr_3CHClOC_2H_5 + Zn = CBr_2{:}CHOC_2H_5 + ZnClBr$.

α,β,β,β-Tetrabromodiethyl Ether.—This ether was prepared by carrying bromine vapor into the cold dibromovinyl ether with a stream of carbon dioxide, the bromine adding as calculated; $CBr_2{:}CHOC_2H_5 + Br_2 = CBr_3CHBrOC_2H_5$. The tetrabromo ether is much less stable than the corresponding tetrachloro ether and there is considerabledecom position when it is distilled at reduced pressure. An alcoholic solution of this ether reacted with granulated zinc to form the vinyl ether; as in the case of the tetrachloro ether, two halogen atoms were removed by the zinc and no hydrogen bromide. No hydrogen was evolved and no acetal formation was detected; $CBr_3CHBrOC_2H_5 + Zn = CBr_2{:}CHOC_2H_5 + ZnBr_2$.

α-Bromo-β-bromo-β,β-dichlorodiethyl Ether.—By the addition of bromine to dichlorovinyl ether, this dibromodichloro ether was obtained and its reactivity to zinc tested; $CCl_2{:}CHOC_2H_5 + Br_2 = CCl_2BrCHBrOC_2H_5$. The compound reacted with zinc at room temperature to form an unsaturated product that was found to be chiefly $CCl_2{:}CHOC_2H_5$ mixed with a small amount of $CClBr{:}CHOC_2H_5$, but the lack of hydrogen formation and the properties of the product showed that the zinc had removed two halogen atoms and not a halogen acid.

Theoretical Part

Four examples have been given of the conversion of halogenated ethers into vinyl ethers by the removal of two halogen atoms by zinc. Other halogenated ethers, such as trichloro ether, dichloro ether and monochloro ether, lose the halogen acid under similar conditions and in alcoholic solution, but the products are acetals. The preparation of dichlorovinyl ether from tetrachloro ether and dichloro-acetal from trichloro ether may be taken as typical of the two reactions. Possible explanations are as follows. (1) The formation of the dichloro-acetal may be due to a direct action between the alpha chlorine atom of the trichloro ether and alcohol in which hydrogen chloride is removed. This reaction is not probable since the alpha chlorine atoms of both trichloro ether and tetrachloro ether show the same degree of reactivity and a direct action with alcohol at a low temperature would not be expected in the one case when it does not occur in the other even at a much higher temperature. Trichloro ether[3] and tetrachloro ether[4] do not react with alcohol at room temperatures, but both ethers form acetals if boiled for several hours with alcohol. When tetrachloro ether reacts with zinc and alcohol, however, no trichloro-acetal is formed. The formation of the acetal in the one case and not in the other could not be due to the catalytic action of zinc or zinc chloride since these substances

[3] Oddo and Mameli, *Gaz. chim. ital.*, [ii] **33**, 412 (1903).

[4] Wurtz and Vogt, *Z. Chem.*, **7**, 680 (1871).

were present in both reactions. (2) Since zinc removes chlorine from one ether and hydrogen chloride from the other, the halogen acid may act as a condensing agent in the acetal formation; but no evidence for this condensing action could be found. The evolution of hydrogen throughout the experiments with trichloro ether indicated that, if any free hydrogen chloride was formed, the amount was very small. Also, hydrogen chloride is absorbed readily by dichlorovinyl ether at room temperatures and alcohol is not. Various tests were made to determine whether or not the presence of hydrogen chloride could cause alcohol addition to the vinyl ether. An alcoholic solution of tetrachloro ether was treated with zinc by the method already described and the solution of dichlorovinyl ether and zinc chloride separated from the zinc. Dry hydrogen chloride was run into samples of this solution and the amounts absorbed, determined by weighings. The quantities absorbed varied from about 5 to 50% of that calculated for the saturation of the dichlorovinyl ether present. If the conversion of the trichloro ether into dichloro-acetal was due to a condensation produced by the hydrogen chloride that might have been present, then the dichlorovinyl ether solutions should have converted entirely in to the acetal. But all the samples tested contained unchanged vinyl ether, the amounts depending upon the quantities of hydrogen chloride that had been run in. The hydrogen chloride had merely added to form trichloro-ether. (3) The acetal formation may be explained by the electronic condition of the vinyl ether at the instant it is released by the removal of hydrogen chloride from a saturated ether.

Reactions of the Double Bonds of Vinyl Ethers.—W. H. Carothers[5] pointed out that the reactions of the double bond could be accounted for by assuming a displacement of electrons to produce parts more or less polar, applying a more general idea proposed by Lewis, Lowry, Noyes[6] and others. He represents active propylene as $CH_3—\overset{*}{C}H—CH_2$, the starred carbon being the "deficient" or positive carbon to which the bromine of hydrogen bromide will attach. The hydrogen of the halogen acid is then drawn to the free electron pair of the negative carbon. A similar addition would be expected if the active propylene molecules are assumed to have the electronic structure $CH_3:\underset{\cdot\cdot}{\overset{\cdot\cdot}{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H$, using the Lewis notation.

H H

If such a state of polarization precedes the addition of a polar molecule, such as hydrogen bromide, to a double bond, then the removal of a halogen acid from a compound should leave the unsaturated product, momentarily, highly polarized. A double bond produced in this manner should be less stable and more likely to form addition products with other polar

[5] Carothers, *J. Am. Chem. Soc.*, **46**, 2226 (1924).

[6] (a) Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916). (b) Lowry, *J. Chem. Soc.*, **123**, 822 (1923). (c) Noyes, *J. Am. Chem. Soc.*, **45**, 2959 (1923).

molecules at the instant it is released than if the unsaturated compound were formed by the removal of two negative atoms. The electronic states of dichlorovinyl ether when formed by the removal of chlorine and hydrogen chloride, respectively, from two chlorinated ethers may be indicated as follows.

$$\overset{Cl\ Cl}{Cl_2\ddot{C}:\ddot{C}HOC_2H_5} + Zn = ZnCl_2 + Cl_2\dot{C}:\dot{C}HOC_2H_5 = Cl_2C::CHOC_2H_5 \qquad (1)$$

$$\overset{H\ Cl}{Cl_2\ddot{C}:\ddot{C}HOC_2H_5} + {}^1/_2\ Zn = {}^1/_2\ ZnCl_2 + H + \overset{H\ OC_2H_5}{Cl_2\ddot{C}:\ddot{C}HOC_2H_5} \qquad (2)$$

$$Cl_2\ddot{C}:CHOC_2H_5 + H:OC_2H_5 = Cl_2\ddot{C}:\ddot{C}HOC_2H_5$$

In Reaction 1 the vinyl ether would not be released in a condition favorable to alcohol addition unless heated; in Reaction 2 its electronic condition would make it more unstable and more reactive to other polar molecules. These reactions illustrate the general mechanism by which zinc removes the halogen or halogen acid from such compounds. The alpha hydrogen atoms never are removed by the metal if there is a halogen atom on this carbon; but beta carbon atoms lose hydrogen, although there may be available halogen atoms present, as in the case of the trichloro ether shown above. The beta hydrogen atoms, therefore, must be nearer the ionic condition and will be released more readily by the transfer of an electron from the zinc. This will leave the hydrogen-bonding pair on the beta carbon atom, as shown above, and the mechanism of alcohol addition will be similar to the addition of a halogen acid to a polarized molecule of an unsaturated hydrocarbon.

Experimental Part

The Action of Zinc on α,β,β,β-Tetrachlorodiethyl Ether.—To test the Neher and Foster reaction, in which zinc removed two chlorine atoms and no hydrogen from this tetrachloro ether, the work was repeated at different temperatures and concentrations. Alcohol concentrations varied from two to six molecular proportions and temperatures from 20° to 75°. The solutions were allowed to stand overnight, water was added, the product distilled with steam, dried and redistilled; b. p., 144°. No hydrogen was evolved, showing that no trichlorovinyl ether was formed. The yields ranged from 70 to 90%, the higher yields being obtained with about six molecular proportions of alcohol. The method was later adopted by a manufacturing chemist for preparing dichlorovinyl ether in quantity.

Preparation and Properties of α,β,β-Trichlorodiethyl Ether.—This ether has been prepared by the chlorination of ether,[3,7] by the addition of chlorine to β-chlorovinyl ether[8] and by heating dichloro-acetal with phosphorus pentachloride.[9]

[7] Jacobsen, *Ber.*, **4**, 217 (1871).

[8] Godefroy, *Jahresber.*, **1886**, 1173.

[9] Krey, *ibid.*, **1876**, 475.

This ether was prepared in a very pure state by running hydrogen chloride into dichlorovinyl ether until a sample tested with bromine showed that saturation was complete. In one experiment, 95 g. of the unsaturated ether required seven hours' running of the hydrogen chloride for saturation. The temperature rose to 35° and remained near this point until saturation was complete. Carbon dioxide was passed through the product until the odor of hydrogen chloride was no longer noticeable. The ether had a rather pleasant odor, similar to that of tetrachloro ether, and was perfectly clear. One hundred and seventeen g. of the trichloro ether was obtained before distillation, the calculated amount being only 115 g. This indicated that the hydrogen chloride had added quantitatively, the extra 2 g. being hydrogen chloride still in solution and not removed by the carbon dioxide. The ether distilled at 77–80° (32–34 mm.); at atmospheric pressure it boiled at 173–175°, chiefly near 174°. In the preparations referred to, Oddo and Mameli obtained a boiling point of 170–175°, Krey found 167° and Godefroy only 157°. The last boiling point indicates that Godefroy may have had the isomer, $CH_2ClCCl_2OC_2H_5$, since the α-substituted ethers show lower boiling points than the β. A density (25°/4°) of 1.3116 was found. Oddo and Mameli found 1.3303 at 14°.

Anal.[10] Subs., 0.1439: Calcd. for $C_4H_7OCl_3$: C, 27.06; H, 3.97; Cl, 59.94. Found: C, 27.19; H, 4.15; Cl, 59.81.

The Action of Zinc on α,β,β-Trichlorodiethyl Ether.—Granulated zinc was added to the pure ether at room temperature. There was an immediate reaction followed by rapid decomposition and an evolution of hydrogen gas. The liberation of hydrogen gas indicated the removal of hydrogen chloride by the zinc, but the dichlorovinyl ether, if formed, was decomposed. Tarry masses were left even when the experiments were repeated at 0° and with a gradual addition of the zinc. The results were the same when the ether was dissolved in 6 molecular proportions of diethyl ether, acetone, ligroin and carbon disulfide and the solutions allowed to react with zinc at room temperatures and at 0°. When the trichloro ether was dissolved in absolute alcohol, however, good yields of dichloro-acetal were obtained. In one experiment, 33 g. of trichloro-ether was dissolved in 48 g. (6 molecular proportions) of alcohol, the flask was cooled in ice water and 43 g. of zinc added. The mixture was kept at about 5° until the action had subsided and then left overnight at room temperature. The alcohol was washed out with water and 27 g. of dried oil obtained. A vacuum distillation at 18–20 mm. gave 4.5 g. at 64–76°, the remainder distilling at 76–79°. The main fraction boiled at 181–184° at atmospheric pressure, this temperature agreeing with the boiling point of dichloro-acetal; yield, 78%.

Anal. Calcd. for $C_6H_{12}O_2Cl_2$: C, 38.62; H, 6.41; Cl, 37.60. Found: C, 38.02; H, 6.47; Cl, 37.91.

Preparation of α-Chloro-β,β,β-tribromodiethyl Ether.—One hundred and fifteen g. of bromal alcoholate, prepared by the addition of alcohol to bromal, was dissolved in 150 cc. of absolute ether. Eighty-five g. of phosphorus pentachloride was cooled with a freezing mixture, washed twice with cold ether and covered with 100 cc. of ether. The ethereal solution of the bromal alcoholate was then run in slowly from a dropping funnel. The flask was shaken continually and the temperature kept below 15°. Only a slight bromine coloration was noticed at the end of the reaction. The mixture was poured from the excess of phosphorus pentachloride into 1000 g. of crushed ice and stirred until most of the ice had melted. The crude ethereal solution was separated, washed several times with large volumes of water and dried with fused calcium chloride. The

[10] In the analyses of these halogenated ethers, carbon, hydrogen and chlorine were obtained simultaneously by a modification of the Dennstedt method to be reported later.

diethyl ester still present was distilled and the heavy oil fractionated at reduced pressure. Ninety-seven g. of the chlorotribromo ether, b. p. 117–122° (13–14 mm.), was obtained; yield, 80%. The ether boiled at 120–121.5° (corr.) (14 mm.) at atmospheric pressure, it decomposed below the boiling point; $d_4^{20.5}$, 2.2069. The molecular weight was determined by the cryoscopic method, using benzene as a solvent.

Anal. Calcd. for $C_4H_6OBr_3Cl$: Hal., 79.74. Found: 79.87.

Mol. wt. Calcd. for $C_4H_6OBr_3Cl$: 345.5. Found: 330.

Preparation of β,β-Dibromovinylethyl Ether.—Fifty-nine g. of the chlorotribromo ether, prepared as described above, was dissolved in absolute alcohol (6 molecular proportions) and 59 g. of granulated zinc added. The reaction began at room temperature and was kept below 30° by cooling under the tap. No gas was evolved and the solution remained entirely colorless. The mixture was allowed to stand for several hours at room temperature, a liter of water was added, the product distilled with steam, dried over calcium chloride and redistilled at reduced pressure. At 14.5–15 mm., 5 g. was obtained at 69–73° and 26 g. at 73–75°; yield, 78%. The product decomposed when heated at atmospheric pressure; b. p., 73–75° (corr.) (15 mm.); $d_4^{17.5}$, 1.7697.

Anal. Calcd. for $C_4H_6OBr_2$: Br, 69.57. Found: 69.03.

Preparation and Properties of α,β,β,β-Tetrabromodiethyl Ether.—Twenty-five g. of the dibromovinyl ether described above was cooled in a U-tube surrounded by a freezing mixture. This tube was connected to another U-tube containing cold bromine. Bromine vapor was driven into the vinyl ether by a stream of carbon dioxide until a slight coloration indicated an excess of the bromine, this excess being absorbed by adding two or three drops more of the vinyl ether; 41.5 g. of the tetrabromo ether was obtained, the calculated amount being 42.4 g. This indicated that the bromine had added quantitatively, the slight loss in weight being due to the evaporation of some of the liquid by the rapid stream of carbon dioxide.

The ether decomposed rapidly when attempts were made to determine its boiling point. At 16 mm. it distilled at 130–140°, the distillate smelling strongly of hydrogen bromide and showing traces of an unsaturated compound. Since no solvent was used in the preparation of the ether, no by-products were formed and the bromine added quantitatively; a sample before distillation was considered as more suited to an accurate density determination and to tests with zinc; $d_4^{17.5}$, 2.2432.

Action with Zinc.—An alcoholic solution of the tetrabromo ether was tested with zinc in exactly the same manner as that described for the chlorotribromo ether. Twenty g. of the ether gave 8 g. of an unsaturated compound boiling at 76–80° (17–18.5 mm.). This indicated the formation of dibromovinyl ether, whose boiling point had been found to be 73–75° (14.5–15 mm.). Since the properties of dibromovinyl ether had been determined in the former preparation, a molecular-weight determination was made to be sure that the unsaturated compound was not tribromovinyl ether formed by the removal of hydrogen bromide by the zinc. A molecular weight of 219 was found by the cryoscopic method, using benzene as a solvent; calcd. for dibromovinyl ether, 230; for tribromovinyl ether, 309. Also, if the tribromovinyl ether had been formed the boiling point would have been much higher than that found.

Preparation and Properties of α-Bromo-β-bromo-β,β-dichlorodiethyl Ether.—Oddo and Mameli[3] prepared this ether by adding a chloroform solution of bromine to dichlorovinyl ether. Since the dichlorovinyl ether is very stable it was thought that a purer product, free of solvent and by-products, could be formed by the direct addition of bromine. Seventy g. of the vinyl ether was placed in a 500cc. flask and the bromine added through a dropping funnel. The cork carried also a thermometer, a calcium chloride tube and a tube for running in carbon dioxide. The ether was stirred by a rapid stream of carbon dioxide while the bromine was being added and the temperature was

kept between 8° and 15°. A slight coloration, which indicated saturation, was removed by the addition of two or three drops of the vinyl ether. The product weighed 148 g., the calculated yield being 149.5. Distillation at 16–16.5 mm. gave 9 g. below 107° and the remainder distilled at 107–108° with only slight decomposition; yield, 93%. Decomposition was rapid when the ether was boiled at atmospheric pressure, the distillate fumed in air and decolorized a carbon tetrachloride solution of bromine. The ether boiled at 106.5–108° (corr.) (16 mm.), with little decomposition; $d_4^{18.5}$, 1.8249. Oddo and Mameli found a boiling point of 124–129° (25–30 mm.).

Anal. Calcd. for $C_4H_6OBr_2Cl_2$: H, 2.02; C, 15.9; Hal., 76.74. Found: H, 2.21; C, 15.9; Hal., 76.6.

Action with Zinc.—Thirty-nine g. of the dibromodichloro ether was dissolved in 80 cc. of absolute alcohol and 40 g. of zinc added. The action was rapid and the flask was cooled under the tap to keep the temperature below 40°. After distilling with steam and drying the oil, 16.5 g. of an unsaturated product was obtained. This was redistilled at atmospheric pressure and 11 g. collected at 143–147° and 3 g. at 147–155°; both fractions absorbed bromine readily. A few drops of the 143–147° fraction were decomposed by molten sodium and a qualitative test indicated only chlorine. Also, the unsaturation of the product and its boiling point showed it to be chiefly dichlorovinyl ether, $CCl_2{:}CHOC_2H_5$; b. p., 144.2°. The removal of a halogen acid by the zinc would have produced either a vinyl ether or an acetal containing three halogen atoms and the boiling point would have been considerably higher than that of the fractions collected. The properties of the product showed that the zinc had removed two halogen atoms and not a halogen acid, which was the sole object of the test.

Summary

Three new halogenated diethyl ethers have been prepared and their properties determined: α-chloro-β,β,β-tribromodiethyl ether, β,β-dibromovinylethyl ether and α,β,β,β-tetrabromodiethyl ether. Pure α-bromo-β-bromo-β,β-dichlorodiethyl ether has been prepared by a modification of an older method. New methods for the preparation of α,β,β-trichlorodiethyl ether and β,β-dichloro-acetal are given.

Typical examples of the reactions of alcoholic solutions of halogenated ethers with zinc are given. The action of zinc has been found to be entirely selective in the removal of two atoms of the halogen or the halogen acid from a given ether. The mechanisms of these reactions have been studied. Beta hydrogen atoms are removed by zinc more readily than beta halogen atoms, but alpha halogen atoms are much more reactive than alpha hydrogen atoms.

The removal of two atoms of a halogen from halogenated ethers in alcohol solution results in the quantitative formation of vinyl ethers but, under the same conditions, the removal of the halogen acid from halogenated ethers containing one less halogen atom in each case does not result in the formation of the same vinyl ethers, as had been expected, but of the corresponding acetals. Various tests indicated that the acetal formation was due to the alcohol addition to the unsaturated ether after the removal of the halogen acid by the direct action of zinc on the saturated ether. The

assumption is made, in explaining these facts, that the removal of the halogen acid leaves the double bond of the vinyl ether in a polarized condition that is more favorable to the addition of other polar molecules, such as alcohol, than if the vinyl ether were prepared by the removal of two halogen atoms.